Energetic and chemical reactivity of atomic and molecular oxygen

To understand their chemical reactivity of atomic and molecular oxygen, it is necessary to look at the electronic configuration of oxygen[1]. The discussion of the states of atomic oxygen is of limited practical use because most oxygen is in the form of molecular oxygen (O_2) at room temperature. Nevertheless, it is interesting to examine the energy diagram of the oxygen atom because similarities with the energy diagram of molecular oxygen can also be used to explain the reactivity of molecular oxygen.

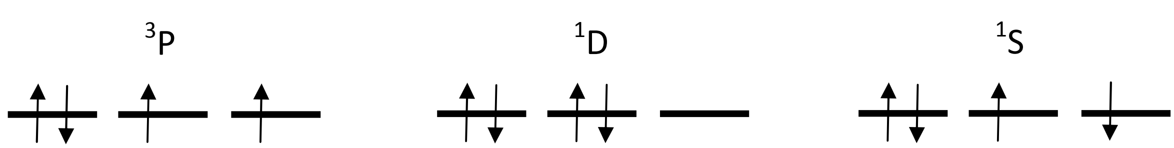
1. Free radicals

In chemistry, a *radical* (also referred to as *free radical*) is an atom, molecule or ion with at least one unpaired electron. The unpaired electron usually cause them to be highly chemically reactive. The radical site is usually noted by putting a dot on the atom (ex.: $^{\bullet}OH$). Although radicals are generally short-lived due to their reactivity, long-lived radicals (such as molecular oxygen) also exists. Radicals plays important roles in several chemical and biological processes.

2. Atomic oxygen

Atomic oxygen has a total of eight electrons. Using the electronic orbitals and the Pauli exclusion principle to fill the orbitals with electrons, the electronic configuration of atomic oxygen is $1s^2 2s^2 2p^4$. Since the 2p orbitals are partially filled, there are three different ways to arrange the electrons in the $2p_x$, $2p_y$ and $2p_z$ orbitals (Figure 1). According to *Hund's first rule*, the ground state configuration corresponds to an orbital occupancy that gives the highest multiplicity[1]. The first configuration has a multiplicity of 3 (hence termed triplet), and the other configurations have a multiplicity of 1 (hence termed singlet). Therefore, the ground state of atomic oxygen has two unpaired electrons (bi-radical), and is designated as ^3P ("triplet P") state. The *Hund's second rule* states that for two configurations with the same multiplicity, the configuration with the highest total orbital angular momentum (L) has the lowest energy. Since the second configuration has the higher L value, its energy is lower. It is the first excited state of atomic oxygen, designated as the ^1D ("singlet D") state. The configuration ^1S is the second excited state.

Figure 1: Electronic configurations ^3P, ^1D and ^1S of the partially filled 2p orbitals of atomic oxygen.



[1] The multiplicity is given by 2S+1, where S is the spin. The spin of an electron is (+/-) 1/2.

The presence of two unpaired electrons gives ^{3}P oxygen two reactive sites that are used to form bounds with other atoms or molecules. The O-H bound energy is ~103 kcal/mol in $^{\bullet}$OH and ~119 kcal/mol in H_2O, whereas typical C-H bond energies are ~100 kcal/mol[1]. Therefore, ^{3}P ground state oxygen reacts readily to abstract a hydrogen atom from the C-H bound of hydrogen-containing molecules. Aside from hydrogen atom abstraction, atomic oxygen may also react directly with molecules that have no unpaired electrons. These reactions are not favored, because they violate the principle of spin conservation. However, the first excited state of atomic oxygen (^{1}D) has one 2p empty orbital. In this case, the ^{1}D excited molecule is more electrophilic and prone to undergo bond-forming addition reactions than the triplet ground state. One example in the radiolysis of water is the reaction[2]:

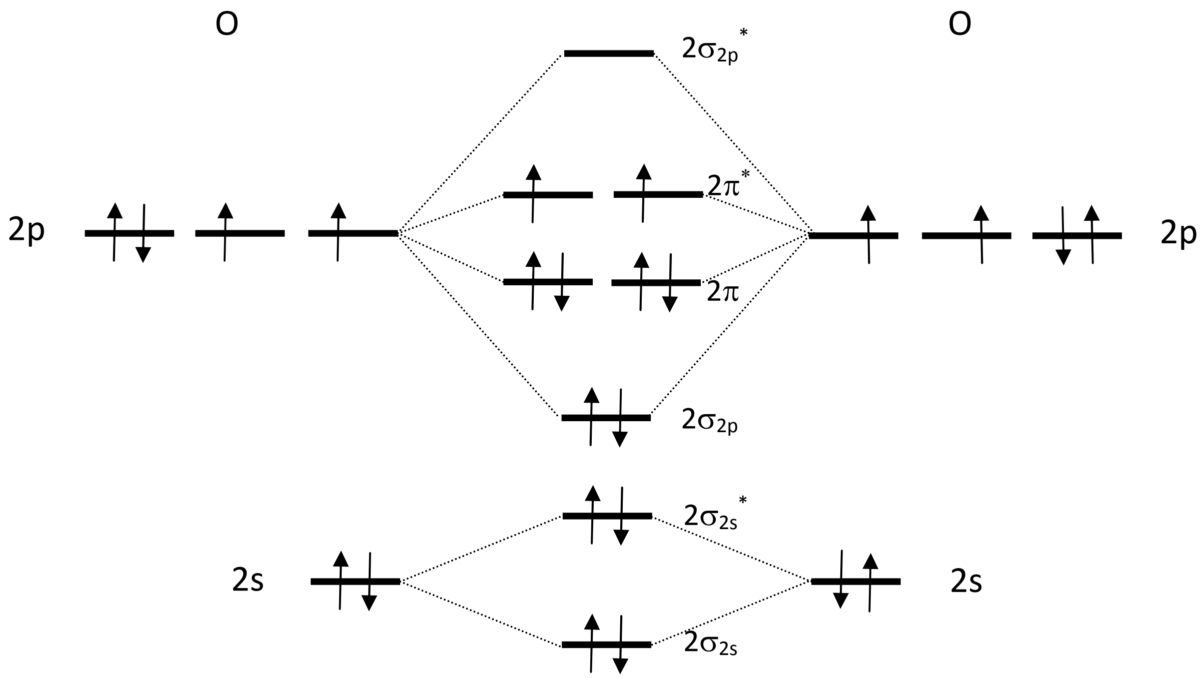
$$O(^1D) + H_2O \rightarrow H_2O_2 \qquad (1)$$

3. Molecular oxygen

Analysis of the reactivity of the molecular oxygen uses similar arguments. The molecular orbital diagram can be constructed from the molecular orbital theory (Figure 2). In molecular oxygen, there are 16 electrons which can be placed into the molecular orbitals to give the electronic configuration: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2\,(\sigma^*_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$. This electronic configuration shows that there is a double bound between the two oxygen atoms. This electron configuration also shows that the π^*_{2p} orbital are each only half filled. As with atomic oxygen, there are three different states corresponding to different arrangement of these electrons. These states are $^3\Sigma^+_g$, $^1\Delta_g$ and $^1\Sigma^-_g$. The ground-state of molecular oxygen is the triplet state ($^3\Sigma^+_g$) and is analog to the ^{3}P state of atomic oxygen. Therefore, molecular oxygen is a bi-radical.

As a result of spin restrictions, many reactions with molecular oxygen are experimentally very slow, even if they are strongly thermodynamically favorable. This supposition is usually true regarding organic substances, but there are important examples in nature and in the laboratory in which oxygenation of substrate occurs at appreciable rates under certain conditions. Moreover, contrary to the ^{3}P atomic oxygen, ($^3\Sigma^+_g$) is not highly reactive as a hydrogen atom abstractor, because the O-H bound energy in $HO_2^{\bullet}$ is relatively low (47 kcal/mol).

Figure 2: Molecular oxygen energetic diagram of O_2.



References

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2. TAUBE, H. 1957. Photochemical reactions of ozone in solution. *Trans. Farad. Soc.* **53**, 656-665. http://dx.doi.org/10.1039/TF9575300656